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FISHING LINE

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[There are no amendments to this patent.]

Abstract

Objective

A type of fishing line characterized by the fact that the fishing line is made of a fiber that is composed of a polyvinyl alcohol-based polymer with an average degree of polymerization in the range of 1500-8000 and starch, with a ratio by weight of said polyvinyl alcohol-based polymer to starch in the range of 90/10-50/50, and which has a tensile strength of 5 g/d or higher and an initial tensile modulus of 150 g/d or higher.

Effects

A type of fishing line is provided characterized by the fact that it has excellent characteristics, including a tensile strength of 5 g/d or higher and an initial tensile modulus of 150 g/d or higher, and, when it is disposed of in soil, the sea, or other natural environments after use, biodegradation takes place due to bacteria and [other] microbes, and no environmental pollution takes place.

Claims

1. A type of fishing line characterized by the fact that the fishing line is made of a fiber that is composed of a polyvinyl alcohol-based polymer with an average degree of polymerization in the range of 1500-8000 and starch, with a ratio by weight of said polyvinyl alcohol-based polymer to starch in the range of 90/10-50/50, and which has a tensile strength of 5 g/d or higher and an initial tensile modulus of 150 g/d or higher.

2. The fishing line described in Claim 1 characterized by the fact that the fibers are twisted multifilaments with their surfaces covered by one or several types of resins selected from among polycaprolactone, polyhydroxy alkanoate-based polymer, and aliphatic polyester.

Detailed explanation of the invention

[0001]

Industrial application field

This invention pertains to a type of fishing line. More specifically, this invention pertains to a type of fishing line made from biodegradable fibers.

[0002]

Prior art

In recent years, people have become more concerned about environmental pollution due to increasing amounts of trash. As a result, processing and disposal of plastic wastes have become a serious societal problem.

[0003]

In order to solve the aforementioned societal problem, demand has developed for degradable plastics that can be decomposed by bacteria, microbes, etc. (biodegradation), or by UV light, etc.

[0004]

Fishing line is one of the objects pertaining to the problem of disposal of wastes into the environment. Consequently, it is necessary to make fishing line from biodegradable fibers to meet the aforementioned demand.

[0005]

As a well known example of fibers containing starch, Japanese Kokai Patent Application No. Sho 55[1980]-116814 discloses a type of rayon fiber characterized by the fact that its dyeability is improved by its comprising a prescribed type of alkaline starch. Also, Japanese Kokoku Patent No. Sho 60[1985]-35480 discloses a method for manufacturing paper containing starch fibers. However, these prior art examples are entirely different from the feed materials used in the present invention.

[0006]

Problems to be solved by the invention

The objective of this invention is to provide a type of fishing line characterized by the fact that it is made from biodegradable fibers composed of a novel PVA-based polymer and starch and, when the used fishing line is disposed of into soil, the sea, or other natural environments, it biodegrades due to bacteria, microbes, etc. so that no environmental pollution takes place.

[0007]

Means to solve the problems

In order to solve the aforementioned problem, the fishing line of this invention has the following constitution: the fishing line is made of a fiber that is composed of a polyvinyl alcohol-

based polymer with an average degree of polymerization in the range of 1500-8000 and starch, with a ratio by weight of said polyvinyl alcohol-based polymer to starch in the range of 90/10-50/50, and which has a tensile strength of 5 g/d or higher and an initial tensile modulus of 150 g/d or higher.

[0008]

For the PVA-based polymer used in this invention, the average degree of polymerization should be in the range of 1500-8000, or preferably in the range of 1500-5000, taking into consideration the desired tensile strength of the fibers obtained and the cost of the polymer actually available.

[0009]

Also, as long as the solubility in solvent is not hampered, copolymerization can be performed with a certain amount of ethylene, acrylic acid, acrylonitrile, etc.

[0010]

There is no special limitation on the type of starch. Examples of starch that can be used include potato starch, corn starch, wheat starch, tapioca starch, sweet maize starch, etc.

[0011]

The tensile strength of the fibers made from said PVA and starch should meet the requirements for a fishing line. For the same strength, the finer the yarn, the better the effect. Consequently, in order to get a better effect, a higher strength is preferred. For the fishing line of this invention, the tensile strength should be in the range of 5 g/d or higher, or preferably 6 g/d or higher.

[0012]

If the tensile strength of the fibers is lower than 5 g/d, the strength becomes insufficient to meet the application requirements, and the aforementioned effect cannot be realized. This is undesirable.

[0013]

As far as the initial tensile modulus of the fibers is concerned, if it is lower than 150 g/d, the yarn becomes insufficiently rigid, and it becomes impossible to transmit the weak signal of fish on the hook to the hands of the fisherman and the fishing rod. This is undesirable for a fishing line.

[0014]

The fibers used in this invention are made of said PVA-based polymer and starch, with a mixing ratio in the range of 90/10-50/50 wt%, or preferably in the range of 85/15-60/40 wt%. If the starch content is less than 10 wt%, the yarn obtained has higher strength and higher initial tensile modulus, yet the time for biodegradation becomes very long, and the objective of this invention cannot be achieved. On the other hand, if the starch content is over 50 wt%, the fibers obtained become very brittle, and the strength and initial tensile modulus are very low. Such a fishing line may not last long in use. This is undesirable.

[0015]

The mixing ratio of PVA-based polymer and starch is selected to be in the range of 90/10-50/50 wt% taking into consideration the desired biodegradation time.

[0016]

When the fibers obtained are multifilaments, a resin is usually applied to the surface after they are twisted for fixation. According to this invention, a twist of 5-30 turns, or preferably 5-20 turns, per 10 cm is desired for realizing the characteristics and quality required for fishing line.

[0017]

Because the objective of this invention is to achieve biodegradation quickly, it is preferred that the surface be coated with a biodegradable resin after twisting of the multifilaments. Such a resin can biodegrade in the environment. Examples include polycaprolactone, polyhydroxy alkanoate-based polymer, aliphatic polyester, etc.

[0018]

As far as the method for manufacturing the fibers used in this invention is concerned, melt extrusion of PVA and starch is difficult because of the decomposition temperature. A preferred method for manufacturing the fibers used in this invention is the solution spinning method in which PVA and starch are dissolved in an appropriate solvent and the solution is extruded from a nozzle, followed by removal of the solvent. In this method, examples of the solvents for preparing the spinning feed liquid include water or dimethyl sulfoxide (hereinafter referred to as DMSO) that can dissolve both PVA and starch, or a mixed solution of them.

[0019]

A specific example of the solution spinning method will be explained in the following. First of all, PVA with a polymerization degree of 1500-8000 and starch are mixed in a ratio of

90/10-50/50 wt% and the mixture is dispersed in a solvent, with the feed liquid concentration being in the range of 10-40 wt%. After heating to 80-120°C for dissolution, a liquid feed dope is obtained. At this time, the viscosity of the feed liquid depends on the degree of polymerization of the PVA, the concentration of the feed liquid, and the mixing ratio of PVA and starch. From the standpoint of spinnability in the subsequent spinning operation, the viscosity should be in the range of 1000-4000 poise at 60°C.

[0020]

The hydrogen ion concentration (pH) of the feed liquid is important to effective prevention of feed component decomposition. Here, starch decomposition from cutting of ether bonds occurs in the low pH region of 6 or less (high acidity). On the other hand, PVA decomposition from cutting of molecular chains occurs in the high pH region of 9 or more (high alkalinity). Taking into consideration these characteristics, it is preferred for the pH value to be kept in the range of 6-9. Then, using the liquid feed dope, fibers are formed using the conventional solution spinning method. In the dry spinning method, the polymer ejected from the nozzle enters an atmosphere hotter than the boiling point of the solvent in which the polymer is dissolved, and the solvent is removed (drying). On the other hand, in the wet spinning method, the polymer is ejected into a nonsolvent [bath] to remove the solvent and cause coagulation. In the dry/wet spinning method, the polymer ejected from the nozzle is first allowed to pass through a vapor phase section, and it is then introduced into a coagulation bath. Any of these methods can be adopted. In the following, an example of the manufacturing method will be explained with reference to the situation where a conventional dry spinning device is used and water is the solvent.

[0021]

First of all, the following operation is performed to improve the spinnability of the liquid feed dope: from a spinning nozzle kept at about 80-120°C, the polymer is ejected into an atmosphere at 110-140°C (with spinning draft [ratio] preferably in the range of 0.5-4.0) to remove the solvent. An appropriate cold drawing is then performed, followed by drawing and heat treatment in an air or nitrogen atmosphere at 200-240°C, with an overall draw ratio in the range of 8-14.

[0022]

Application examples

This invention will be explained in detail in the following with reference to application examples. In the application examples, characteristics were measured as follows.

[0023]

<Strength and elongation of fibers>

Measurement was performed according to JIS L 1017.

[0024]

In this regard, after the fiber sample was stored for 24 h in a room with temperature and humidity adjusted to 20°C and 65% RH, the sample, twisted 10 turns for every 10 cm, was tested on a "Tensilon" DTM-4L model tensile tester (product of Toyo Baldwin Co., Ltd.) using a test length of 25 cm and at a tensile [crosshead] speed of 30 cm/min. Pneumatic jaws for cords were used for the chucks.

[0025]

<Strength retention of fibers in soil>

A fiber sample was buried in soil. After a prescribed number of days, it was taken out, and the residual strength was measured using the aforementioned method, and the strength retention was calculated.

[0026]

Application Example 1

PVA, with a degree of polymerization of 1800 and a degree of saponification of 99.9 mol%, and starch (corn starch) were mixed together in a ratio by weight of 70/30. The mixture was dispersed and dissolved in water, for a total polymer concentration of 30 wt%. In this way, a feed liquid was prepared. (90°C)

The feed liquid was then ejected from a nozzle with 50 holes 0.1 mm in diameter and kept at 100°C. The water solvent was removed (dried) in an atmosphere kept at 130°C, followed by cold drawing for a draw ratio of about 3, and then drawing in an air atmosphere at 230°C for a draw ratio of 3.8. The fibers were then wound up. For the fibers obtained, the filament size was 3.7 d, the tensile strength was 5.9 g/d, and the elongation was 4.6%.

[0027]

The fibers, twisted for 10 turns/10 cm, were then dipped in melted polycaprolactone (hereinafter referred to as PCL) to coat the surface.

[0028]

The sample was buried in soil to a depth of 10 cm, and the strength retention was measured. It was found that the strength retention was 94% after 12 months, and it was 42% after 18 months. It is clear that the strength of the fibers decreased due to decomposition.

[0029]

Application Example 2

PVA, with degree of polymerization of 2300 and a degree of saponification of 99.9 mol%, and starch (corn starch) were mixed together in a ratio by weight of 60/40. The mixture was dispersed and dissolved in water, for a total polymer concentration of 25 wt%. In this way, a feed liquid was prepared.

[0030]

The feed liquid was then ejected from a nozzle with 50 holes 0.1 mm in diameter and kept at 110°C. The water solvent was removed in an atmosphere kept at 130°C, followed by cold drawing for a draw ratio of about 2.5, and then drawing in an air atmosphere at 220°C for a draw ratio of 3.4. The fibers were then wound up. For the fibers obtained, the filament size was 3.8 d, the tensile strength was 5.1 g/d, and the elongation was 4.1%.

[0031]

PCL was then coated on the surface to form a sample for evaluation as was described for Application Example 1. The sample was buried in soil to a depth of 10 cm, and the strength retention was measured. It was found that the strength retention was 72% after 12 months, and it was 14% after 18 months. It is clear that the strength of the fibers decreased significantly due to decomposition.

[0032]

Comparative Example 1

PVA, with degree of polymerization of 2600 and a degree of saponification of 99.9 mol%, and starch (corn starch) were mixed together at a ratio by weight of 98/2. The mixture was dispersed and dissolved in water, for a total polymer concentration of 24 wt%. In this way, a feed liquid was prepared.

[0033]

The feed liquid was then ejected from a nozzle with 50 holes 0.12 mm in diameter and kept at 105°C. The water solvent was removed in an atmosphere kept at 140°C followed by cold

drawing for a draw ratio of about 3, and then drawing in an air atmosphere at 230°C for a draw ratio of 4.4. The fibers were then wound up. For the fibers obtained, the filament size was 3.2 d, the tensile strength was 15.3 g/d, and the elongation was 4.8%.

[0034]

PCL was then coated on the surface to form a sample for evaluation as was described for Application Example 1. The sample was buried in soil to a depth of 10 cm, and the strength retention was measured. It was found that although decomposition of PCL on the surface of the fibers took place, the strength retention was nevertheless high; that is, it was 98% after 12 months, and 95% after 18 months. It is clear that there is little decrease in strength of the fibers in the soil.

[0035]

Comparative Example 2

PVA, with degree of polymerization of 2600 and a degree of saponification of 99.5 mol%, and starch (corn starch) were mixed together at a ratio by weight of 40/60. The mixture was dispersed and dissolved in water, for a total polymer concentration of 23 wt%. In this way, a feed liquid was prepared.

[0036]

The feed liquid was then ejected from a nozzle with 50 holes 0.12 mm in diameter and kept at 120°C. The water solvent was removed in an atmosphere kept at 130°C, followed by cold drawing. However, drawing could only be performed for a draw ratio as low as about 1.8. Also, sufficient drawing could not be achieved in the dry hot drawing performed after the cold drawing.

[0037]

Application Example 3

PVA, with degree of polymerization of 4200 and a degree of saponification of 99.9 mol%, and starch (corn starch) were mixed together at a ratio by weight of 85/15. The mixture was dispersed and dissolved in water, for a total polymer concentration of 24 wt%. In this way, a feed liquid was prepared.

[0038]

The feed liquid was then ejected from a nozzle with 50 holes 0.1 mm in diameter and kept at 130°C. The water solvent was removed in an atmosphere kept at 140°C, followed by cold

drawing for a draw ratio of about 2.7, and then drawing in an air atmosphere at 235°C for a draw ratio of 5.2. The fibers were then wound up. For the fibers obtained, the filament size was 2.6 d, the tensile strength was 15.1 g/d, and the elongation was 4.6%.

[0039]

PCL was then coated on the surface to form a sample for evaluation as was described for Application Example 1. The sample was buried in soil to a depth of 10 cm, and the strength retention was measured. It was found that the strength retention was 96% after 12 months, and it was 55% after 18 months. It is clear that the strength of the fibers decreased significantly due to decomposition.

[0040]

Application Example 4

PVA, with degree of polymerization of 6000 and a degree of saponification of 99.9 mol%, and starch (corn starch) were mixed together at a ratio by weight of 60/40. The mixture was dispersed and dissolved in water, for a total polymer concentration of 20 wt%. In this way, a feed liquid was prepared.

[0041]

The feed liquid was then ejected from a nozzle with 50 holes 0.08 mm in diameter and kept at 130°C. The water solvent was removed in an atmosphere kept at 130°C, followed by cold drawing for a draw ratio of about 2.7, and then drawing in an air atmosphere at 240°C for a draw ratio of 5.4. The fibers were then wound up. For the fibers obtained, the filament size was 2.2 d, the tensile strength was 14.1 g/d, and the elongation was 4.9%.

[0042]

PCL was then coated on the surface to form a sample for evaluation as was described for Application Example 1. The sample was buried in soil to a depth of 10 cm, and the strength retention was measured. It was found that the strength retention was 81% after 12 months, and it was 24% after 18 months. It is clear that the strength of the fibers decreased significantly due to decomposition.

[0043]

Effects of the invention

The fishing line of this invention has the good mechanical characteristics required for a fishing line, and it is also biodegradable. When used fishing line is disposed of in soil or the sea,

biodegradation takes place due to bacteria, microbes, etc. Consequently, no environmental pollution results.